SUPPORTING INFORMATION

Synthesis and Magnetic Properties of a New Family of Macrocyclic $M^{II}_3Ln^{III}$ Complexes: Insights into the Effect of Subtle Chemical Modification on Single Molecule Magnet Behavior

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Liviu F. Chibotaru,* Annie K. Powell* and Sally Brooker*

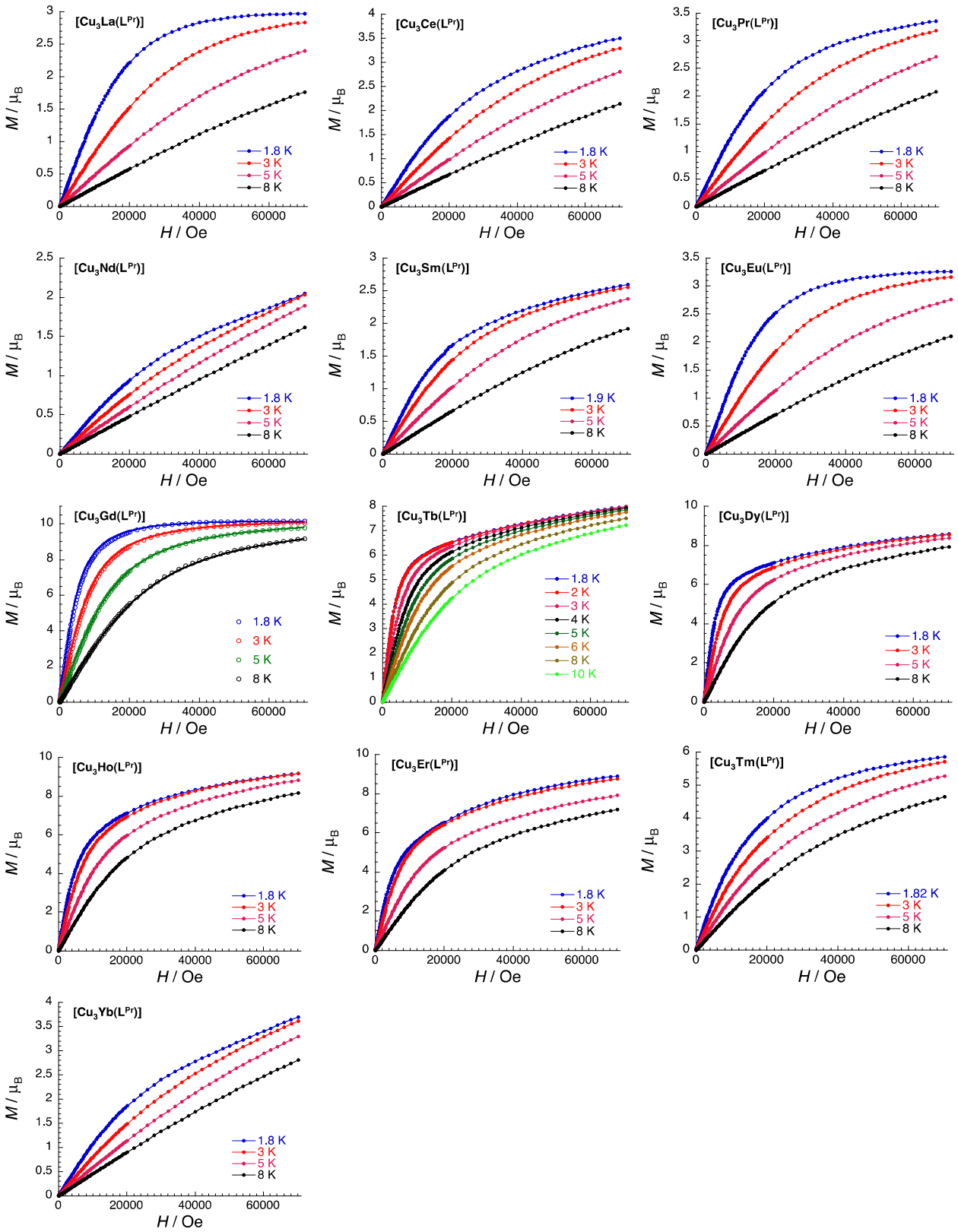


Figure S1: Field dependence of magnetization for $Cu_3Ln(\mathbf{L^{Pr}})(NO_3)_3{\cdot}x$solvents where Ln = La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm or Yb. The solid lines are a guide for the eye.

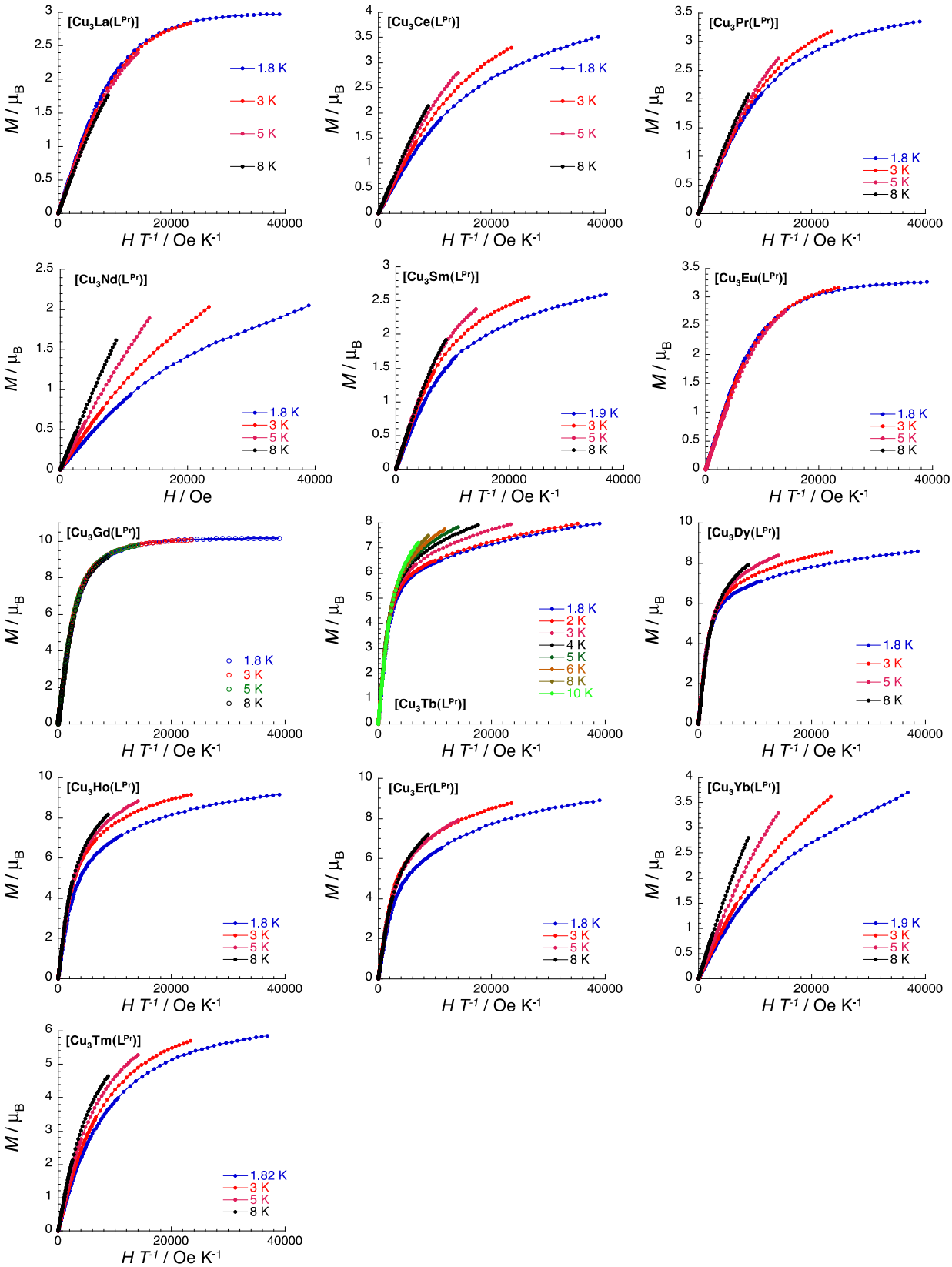


Figure S2: *M* vs *H/T* plots at the indicated temperatures for $Cu_3Ln(\mathbf{L^{Pr}})(NO_3)_3{\cdot}x$solvents where Ln = La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm or Yb). The solid lines are a guide for the eye.

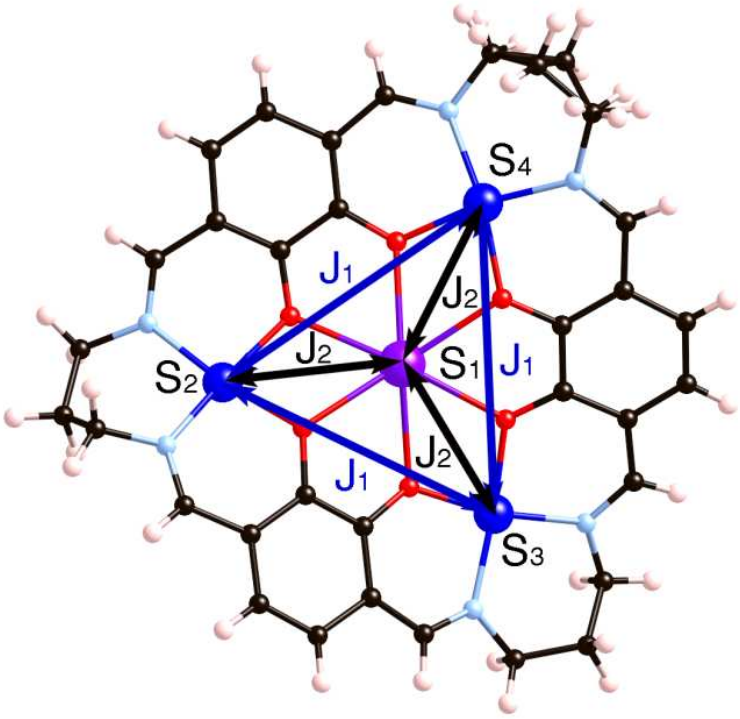


Figure S3: Scheme of the spin topology in [$Cu_3Gd(\mathbf{L}^{Pr})$].

Magnetic properties calculated from an *ab initio* approach for the [$Cu_3La(L^{Pr})$], [$Cu_3Tb(L^{Pr})$] and [$Cu_3Dy(L^{Pr})$] complexes

Computational details:
Basis Sets: All employed basis sets were taken from the standard ANO-RCC basis set library from MOLCAS. The following contractions were used for the atoms:
Tb, Dy – 8s7p5d4f2g1h.
Zn – 6s5p3d2f1g.
La – La.ECP.deGraaf.0s.0s.0e-La(LaMnO3).
N, O – 4s3p2d1f. (only for the first coordinated atoms, which make a bond with Tb)
C – 4s3p1d. (only for the atoms which are directly bonded to the first coordination sphere of O and N)
N, O, C – 3s2p. (for distant atoms)
H – 3s1p. (only for the atoms which are directly bonded to the first coordination sphere of O and N)
H – 2s. (for distant atoms)

Active space of the CASSCF method included 8 electrons in 7 orbitals for Tb(III) and 9 electrons in 7 orbitals for Dy(III): i.e. all orbitals of the 4f shell.
The **spin orbit interaction** was computed by mixing of 7 septets, 91 quintets, 91 triplets and 26 singlet spin free states for Tb(III), while for the Dy(III) 21 sextets, 128 quartets and 130 doublets were mixed.

The lanthanide-containing fragment was built by replacing Cu atoms by diamagnetic Zn atoms. For Cu fragments smaller model fragments have been employed, due to the necessity of adding the dynamic correlation within the CASPT2 program. Larger fragments require much more computational resources, and become untreatable with CASPT2. Structure of the calculated Cu model fragments is shown in Fig. S5. No geometry optimization on model fragments was done. **Active space** of the CASSCF method for Cu fragments included 9 electrons in 5 orbitals and 7 pairs of double-occupied ligand type orbitals, to account for the ligand-to-metal charge-transfer states, which are known to be important for Cu(II) ions. The **spin orbit interaction** was computed by mixing all computed spin free states.

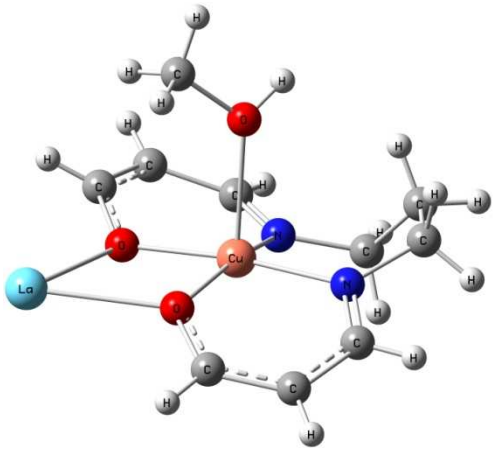


Figure S4: Structure of the calculated Cu(1) fragment. Fragments Cu(2) and Cu(3) have similar structure.

Table S1. Energies (cm^{-1}) of the calculated spin-free and spin orbit states on Ln^{3+} fragments in [Cu_3Tb] and [Cu_3Dy] (Kramers doublets for Dy(III) and singlets in Tb(III)).

Dy(III)			Tb(III)		
Spin multiplicity	**spin-free states (CASSCF)**	**spin-orbit states (KD) (RASSI)**	**Spin multiplicity**	**spin-free states (CASSCF)**	**spin-orbit states (singlets) (RASSI)**
6	0.000	0.000	7	0.000	0.000
	32.116	47.860		31.551	4.248
	84.494	82.686		152.107	59.496
	93.089	219.569		271.389	91.321
	174.854	228.644		342.017	102.018
	189.255	286.363		455.383	153.304
	328.786	320.310		933.597	164.914
	341.669	435.826	5	25694.211	211.549
	488.891	3605.217		25725.471	220.366
	592.656	3642.403		25727.758	264.691
	619.141	3661.137		25819.563	267.049
	7537.912	3752.088		25821.243	472.033
	7669.542	3778.793		29190.999	472.968
	7701.845	3806.416		29197.543	2143.297
	7757.221	3881.573		29215.573	2156.855
	7787.596	6139.932		29224.899	2179.772
	7841.038	6167.502		29276.633	2187.106
	7852.740	6203.544		29292.407	2227.803
	34893.898	6281.749		29313.499	2232.586

	34975.637	6315.609
	35287.165	6380.445
		8088.536
		8117.820
		8178.677
		8267.469
		8326.363
		9619.966
		9652.930
4	24837.177	9711.179
	24848.647	9882.277
	24868.708	10010.986
	24905.400	10067.501
	24916.532	10106.454
	24930.323	10127.009
	24945.895	10142.093
	24980.692	10179.917
	25021.146	10785.026
	25095.711	10889.622
	25103.624	10991.684
	25126.898	11467.957
	25159.958	11514.545
	25174.882	11547.773
	25219.144	11553.683
	25291.211	11579.181
	25315.200	13391.641
	25323.242	13446.141
	25337.450	13493.549
	25341.441	13511.255
	25357.823	14871.257
	…	14918.699
2	37320.539	14931.569
	37329.559	15768.656
	37351.799	15776.724
	37355.167	16302.455
	37360.895	24524.334
	37381.805	24613.666
	37394.811	24655.453
	37414.763	24708.292
	37510.714	24838.577
	37558.835	25132.743
	37593.303	25165.211
	37624.323	25210.466
	37634.442	25286.142
	37666.539	25350.619
	37669.181	25365.143
	37687.634	25391.385
	37690.838	25434.549
	39032.338	27279.697
	39051.839	27293.151
	39072.918	27319.457
	…	…

	29323.259	2311.829
	29441.886	2318.843
	29445.303	2361.694
	29514.636	2446.980
	29523.544	2467.452
	29531.075	3486.670
	29576.874	3519.948
	29580.834	3548.039
	…	3556.790
3	47164.452	3584.061
	47173.110	3622.169
	47175.781	3712.136
	48218.507	3784.083
	48220.181	3907.508
	48245.157	4572.406
	48248.533	4619.160
	48264.424	4644.493
	48271.435	4669.277
	48306.664	4738.732
	48338.742	4760.042
	48349.871	4762.724
	48378.019	5365.076
	48402.226	5392.824
	48422.510	5414.964
	48444.071	5442.046
	48467.844	5557.170
	48481.623	5849.711
	48504.738	5862.298
	48509.791	6063.455
	48610.233	6174.594
	…	23567.727
1	56843.878	23577.714
	57514.401	23581.429
	57515.200	23602.672
	57544.725	23604.299
	57548.313	23619.987
	57593.439	23629.803
	57602.765	23677.345
	57623.563	23680.360
	57644.777	29569.087
	57700.935	29572.021
	57754.446	29576.080
	57771.601	29581.993
	57775.608	29583.566
	57806.555	29585.721
	57843.696	29595.783
	57849.379	30189.740
	57856.264	30190.405
	57876.888	30220.254
	58011.736	30220.671
	58013.119	30263.926
	…	…

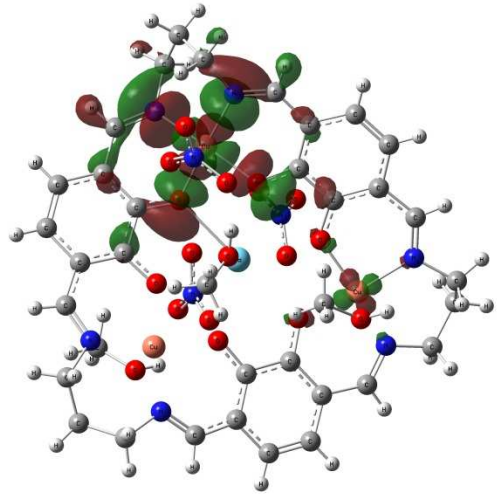
Table S2. Energies (cm^{-1}) of the calculated spin-free and spin orbit states on Cu(II) fragment in [Cu_3Tb].

Spin multiplicity	Spin-free states		
	Cu(1)	Cu(2)	Cu(3)
2	0	0	0
	19375	20073	21965
	19973	20937	22858
	22587	22385	23435
	23140	23364	24038
	38824	37371	25436
	39405	38224	34669
	45132	43221	39444
	46598	45664	40738
	60036	58441	42715
	61952	60019	46273

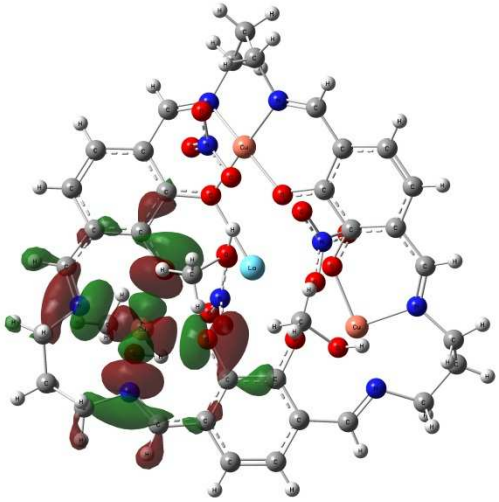
Table S3. Energies (cm^{-1}) of the lowest eight exchange doublets for [Cu_3Tb] and [Cu_3Dy].

ID	$TbCu_3$			$DyCu_3$		
	energy		*g* tensor	energy		*g* tensor
1	0.000000000 0.000000061	g_X g_Y g_Z	0.0702 0.0849 22.5796	0.000000000 0.000016381	g_X g_Y g_Z	0.000 0.000 24.917
2	7.105831985 7.105832040	g_X g_Y g_Z	2.3663 2.7211 16.3099	5.953811290 5.960300619	g_X g_Y g_Z	0.000 0.000 20.749
3	9.064350685 9.064350740	g_X g_Y g_Z	1.0807 1.3485 16.5745	7.017724581 7.021506354	g_X g_Y g_Z	0.000 0.000 20.770
4	9.068533188 9.068533243	g_X g_Y g_Z	1.1312 1.3429 16.4972	7.023486034 7.027240390	g_X g_Y g_Z	0.000 0.000 20.764
5	16.026605734 16.026605790	g_X g_Y g_Z	1.8793 2.6203 11.9709	11.983709338 12.025523475	g_X g_Y g_Z	0.000 0.000 16.589
6	17.920610109 17.920610165	g_X g_Y g_Z	0.9637 1.2247 12.2555	13.065365604 13.069949048	g_X g_Y g_Z	0.000 0.000 0.000
7	17.924340980 17.924341036	g_X g_Y g_Z	0.9765 1.1664 12.1787	13.085995215 13.090601809	g_X g_Y g_Z	0.000 0.000 0.000
8	23.608225957 23.608226021	g_X g_Y g_Z	0.1508 0.1766 9.5883	18.154068612 18.159795052	g_X g_Y g_Z	0.000 0.000 12.438

a)



b)



c)

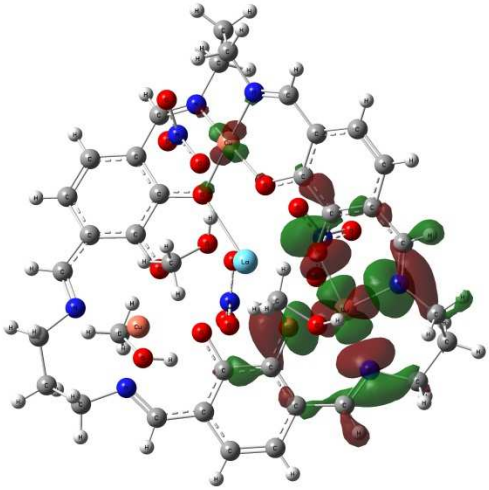


Figure S5. Localized magnetic orbitals on Cu1 (a), Cu2 (b) and Cu3 (c) in the compound $[Cu_3Ce(\mathbf{L}^{\mathbf{Pr}})(NO_3)_2(MeOH)_3](NO_3)$. See the main text for the details.

checkCIF for $[Cu_3Ce(L^{Pr})(NO_3)_3(MeOH)_3]$ (HF459)

Datablock: HF459

```
Bond precision:      C-C = 0.0070 A              Wavelength=0.71073
Cell:        a=10.581(3)     b=13.203(3)    c=15.696(3)
             alpha=80.395(7) beta=78.989(7) gamma=76.952(8)
Temperature: 92 K
                    Calculated                      Reported
Volume              2079.2(9)                       2079.1(8)
Space group         P -1                            P-1
Hall group          -P 1                            ?
Moiety formula      C36 H42 Ce Cu3 N9 O18           C36 H42 Ce Cu3 N9 O18
Sum formula         C36 H42 Ce Cu3 N9 O18           C36 H42 Ce Cu3 N9 O18
Mr                  1219.56                         1219.53
Dx,g cm-3           1.948                           1.948
Z                   2                               2
Mu (mm-1)           2.678                           2.678
F000                1220.0                          1220.0
F000'               1221.92
h,k,lmax            13,16,19                        13,16,19
Nref                8614                            8449
Tmin,Tmax           0.732,0.765                     0.463,0.775
Tmin'               0.398
Correction method= MULTI-SCAN
Data completeness= 0.981        Theta(max)= 26.490
R(reflections)= 0.0427( 6989)      wR2(reflections)= 0.1181( 8449)
S = 1.048              Npar= 604
```

The following ALERTS were generated. Each ALERT has the format
test-name_ALERT_alert-type_alert-level.
Click on the hyperlinks for more details of the test.

Alert level C

PLAT094_ALERT_2_C Ratio of Maximum / Minimum Residual Density 2.57
PLAT125_ALERT_4_C No '_symmetry_space_group_name_Hall' Given ..... ?

Alert level G

PLAT153_ALERT_1_G The su's on the Cell Axes are Equal (x 100000) 300 ang.
PLAT232_ALERT_2_G Hirshfeld Test Diff (M-X) Ce1 -- O30 .. 10.00 su
PLAT232_ALERT_2_G Hirshfeld Test Diff (M-X) Ce1 -- O31 .. 5.44
PLAT794_ALERT_5_G Note: Tentative Bond Valency for Ce1 (III) 3.18
PLAT794_ALERT_5_G Note: Tentative Bond Valency for Cu1 (II) 2.23
PLAT794_ALERT_5_G Note: Tentative Bond Valency for Cu2 (II) 2.35
PLAT794_ALERT_5_G Note: Tentative Bond Valency for Cu3 (II) 2.13

checkCIF for $[Cu_3Dy(L^{Pr})(NO_3)_3(MeOH)_3]$ (HF452)

Datablock: hf452

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Bond precision:      C-C = 0.0115 A              Wavelength=0.71073
Cell:         a=12.1722(14)    b=13.4004(14)  c=14.7438(14)
              alpha=109.487(5) beta=95.676(5) gamma=110.021(5)
Temperature: 92 K
```

	Calculated	Reported
Volume	2067.6(4)	2067.5(4)
Space group	P -1	P-1
Hall group	-P 1	?
Moiety formula	C36 H42 Cu3 Dy N8.25 O15.75, 0.75(N O3)	?
Sum formula	C36 H42 Cu3 Dy N9 O18	C36 H42 Cu3 Dy N9 O18
Mr	1241.94	1241.91
Dx,g cm-3	1.995	1.995
Z	2	2
Mu (mm-1)	3.399	3.399
F000	1236.0	1236.0
F000'	1238.06	
h,k,lmax	15,16,18	15,16,18
Nref	8599	8511
Tmin,Tmax	0.332,0.621	0.227,0.648
Tmin'	0.117	

```
Correction method= MULTI-SCAN
Data completeness= 0.990        Theta(max)= 26.520
R(reflections)= 0.0464( 7326)      wR2(reflections)= 0.1199( 8511)
S = 1.057              Npar= 640
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The following ALERTS were generated. Each ALERT has the format
test-name_ALERT_alert-type_alert-level.
Click on the hyperlinks for more details of the test.

Alert level B

PLAT201_ALERT_2_B Isotropic non-H Atoms in Main Residue(s) 4

Alert level C

PLAT094_ALERT_2_C Ratio of Maximum / Minimum Residual Density 2.14
PLAT230_ALERT_2_C Hirshfeld Test Diff for N5 -- C23 .. 5.17 su
PLAT234_ALERT_4_C Large Hirshfeld Difference C20 -- C21 .. 0.16 Ang.
PLAT234_ALERT_4_C Large Hirshfeld Difference C21 -- C22 .. 0.16 Ang.
PLAT234_ALERT_4_C Large Hirshfeld Difference C28 -- C29 .. 0.17 Ang.
PLAT342_ALERT_3_C Low Bond Precision on C-C Bonds (x 1000) Ang .. 12
PLAT360_ALERT_2_C Short C(sp3)-C(sp3) Bond C20 - C21 ... 1.43 Ang.

Alert level G

PLAT002_ALERT_2_G Number of Distance or Angle Restraints on AtSite 38
PLAT003_ALERT_2_G Number of Uiso or Uij Restrained Atom Sites 4
PLAT063_ALERT_4_G Crystal Size Likely too Large for Beam Size .... 0.62 mm
PLAT083_ALERT_2_G SHELXL Second Parameter in WGHT Unusually Large 9.61
PLAT153_ALERT_1_G The su's on the Cell Axes are Equal (x 100000) 140 Ang.
PLAT154_ALERT_1_G The su's on the Cell Angles are Equal (x 10000) 500 Deg.

PLAT194_ALERT_1_G Missing _cell_measurement_reflns_used datum .... ?
PLAT242_ALERT_2_G Check Low Ueq as Compared to Neighbors for C9B
PLAT242_ALERT_2_G Check Low Ueq as Compared to Neighbors for O70B
PLAT242_ALERT_2_G Check Low Ueq as Compared to Neighbors for N45
PLAT244_ALERT_4_G Low 'Solvent' Ueq as Compared to Neighbors of N40
PLAT301_ALERT_3_G Note: Main Residue Disorder ..... 14 Perc.
PLAT302_ALERT_4_G Note: Anion/Solvent Disorder ..... 100 Perc.
PLAT432_ALERT_2_G Short Inter X...Y Contact O50 .. C1 .. 3.00 Ang.
PLAT432_ALERT_2_G Short Inter X...Y Contact C10B .. O56 .. 2.78 Ang.
PLAT790_ALERT_4_G Centre of Gravity not Within Unit Cell: Resd. # 2
N O3
PLAT811_ALERT_5_G No ADDSYM Analysis: Too Many Excluded Atoms .... !
PLAT860_ALERT_3_G Note: Number of Least-Squares Restraints 127